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# Applications of Vibrational Spectroscopy in the Study of Explosives

by Kevin L. McNesby and Rose A. Pesce-Rodriguez

ARL-RP-62

December 2002

A reprint from the *Handbook of Vibrational Spectroscopy*, J. M. Chalmers and P. R. Griffiths (eds.),  
Chichester, England: John Wiley & Sons Ltd., 2002.

20030103 181

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# Applications of Vibrational Spectroscopy in the Study of Explosives

Kevin L. McNesby and Rose A. Pesce-Rodriguez

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## 1 INTRODUCTION

This article discusses the ways in which vibrational spectroscopy is applied to the study of the class of energetic materials that are commonly called explosives. The article begins with a very brief overview of types and classes of explosives, continues with a few remarks about how a vibrational spectroscopist might approach the study of explosives, discusses some of the most common methods applied to the study of explosives, provides a brief summary of several investigations, and provides a table of vibrational spectroscopic methods and how they have been applied to the study of explosives. A glossary and list of references is also provided. The scientific literature over the last several decades contains thousands of articles dealing with spectroscopy of explosives. Even so, the number of review articles dealing with the applications of vibrational spectroscopy to the study of explosives is limited.<sup>1-3</sup> Our goal in writing this article is to provide an entry point for those interested in the study of vibrational spectroscopy of explosives, and a reference tool to the spectroscopist currently engaged in explosives research.

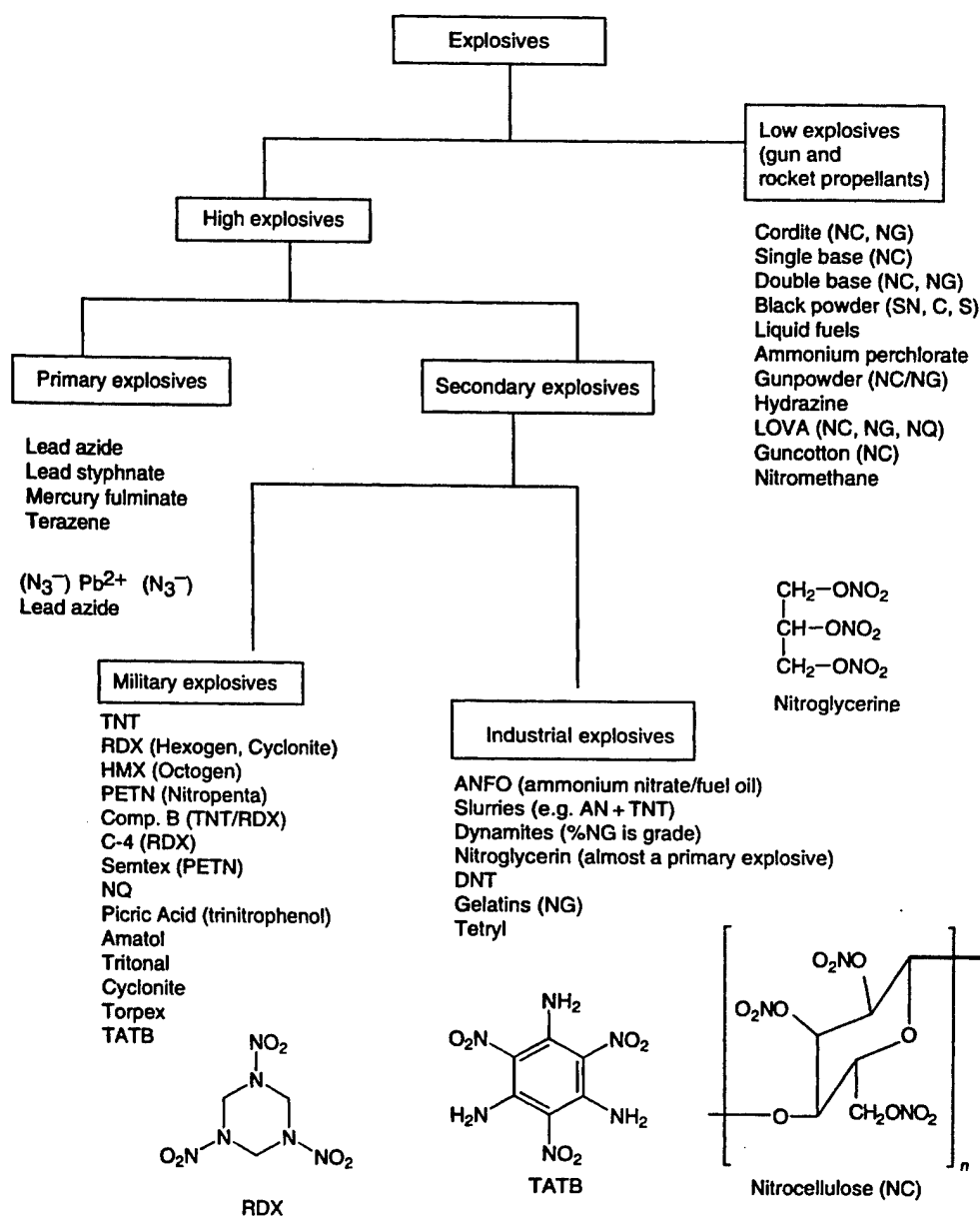
## 2 BACKGROUND ON EXPLOSIVES

Energetic materials of the explosive type are substances (pure, or in mixtures) that, without the participation of external reactants such as air, undergo rapid chemical change to liberate large amounts of heat and gas. Worldwide, there are approximately 150 neat compounds and

formulations used as explosives,<sup>4</sup> with approximately 60% of these being used for commercial applications (mining, construction, sporting), and the remainder used for military applications (guns, warheads, rockets). Explosives may be initiated by mechanical means (e.g. impact, friction), by heat, or by detonating shock. The propagation of reaction in the explosive from the initiating location or site may be slower than the sound velocity (deflagration, such as in gunpowder) or faster than the sound velocity (detonation). Explosives are characterized by several factors. These include their burn or reaction rate, which when combined with degree of confinement, density, and enthalpy of reaction determine brisance. Brisance, or shattering potential, is the destructive fragmentation effect of an explosive on its immediate vicinity.<sup>5</sup> Other factors characterizing an explosive are sensitivity (ease with which chemistry is initiated), and strength (total energy released when reactant changes to product).<sup>5</sup> According to these properties, explosives are usually divided into two main groups: low or deflagrating explosives and high or detonating explosives. Usually, low explosives generate less than 50 000 psi (345 MPa) peak pressures, have burn rates on the order of meters per second, and the pressure-time curve is such that these materials exert a heaving or thrusting action.<sup>4</sup> The group of explosives called propellants fall within the low explosives family. High explosives may generate 100 000 to 500 000 psi (690 to 3448 MPa) peak pressures, and the chemical reaction may occur in a detonation wave that travels through the explosive at several miles per second. High explosives are grouped into primary high explosives (usually used as initiators or primers) and secondary high explosives. Many well known explosive formulations (C-4, Semtex) are classified as secondary high explosives. Most explosives (note, this is not the case for many primary

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**Figure 1.** An abbreviated family tree of explosives (adapted from Kohler and Meyer<sup>5</sup>) and the chemical structure of several low and high explosives.

high explosives) consist of an oxidizer (usually an oxide of nitrogen) and a fuel (usually a hydrocarbon), often in the same molecule. Figure 1 shows an abbreviated family tree of explosives (adapted from Kohler and Meyer)<sup>5</sup> and the chemical structure of several low and high explosives.

### 3 MATERIALS HANDLING

**Any handling of explosives should be done only by personnel specifically trained in their use. Explosive behavior**

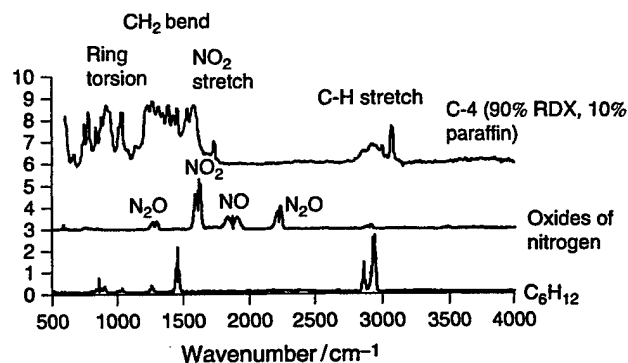
may be unpredictable and special care must be taken when working in unfamiliar surroundings, in environments capable of producing static electrical discharge or which are at elevated temperatures, and in preparing samples which involve confinement or pressure. It should be emphasized that many accidents occur when trained personnel are handling explosives, so caution must always be exercised when using these materials. For primary high explosives (mercury fulminate, lead azide, etc.) special precautions must be exercised. Instruction on handling any material classified as explosive is beyond the scope of this article.

#### 4 VIBRATIONAL SPECTROSCOPY

Vibrational spectra of unreacted explosives are usually measured with the sample in the solid state, mainly because most explosives are solids at room temperature (nitroglycerin being the most well known exception). For high explosives and formulations of high explosives, in which the main ingredient(s) are often crystalline when pure (e.g. TNT, probably the most studied explosive, or PETN, the main ingredient in the explosive formulation Semtex), samples are usually powders or semi-malleable solids. For low explosive formulations and propellants, often containing ingredients which are polymeric when pure (e.g. nitrocellulose), samples are typically grains (compressed or formed in the shape of a right circular cylinder), coarse or fine powders, or solid solutions.

A common misconception is that for spectroscopic studies of explosives, the choice of methods is limited because of the danger of handling the material. There are a large number of articles in the open literature dealing with spectroscopy of primary high explosives,<sup>6-10</sup> and for secondary high explosives (RDX, PETN, etc.), formulations of these explosives (C4, Semtex, etc.), low explosives (nitrocellulose, etc.) and propellant formulations (JA2, M43, etc.), the methods of analysis are almost unlimited. As mentioned above, precautions must be exercised when handling these materials, but for the most part the biggest impediment to measuring the vibrational spectra of explosives is procurement of the sample. This is the main reason that many of the published vibrational spectra are from government and military laboratories, and from university laboratories with long standing collaborations with public sector laboratories.

In our laboratory, we often envision vibrational spectra from the point of view outlined in Hertzberg's 'Spectra of Diatomic Molecules' and 'Infra-red and Raman Spectra'.<sup>11</sup> Figure 2 shows the gas phase infrared absorbance spectrum of cyclohexane ( $C_6H_{12}$ ) and a gas mixture of the simple oxides of nitrogen ( $NO$ ,  $NO_2$ ,  $N_2O$ ), and the infrared photoacoustic spectrum of the solid explosive formulation C-4. C-4 is an explosive formulation made up of approximately 90% RDX and 10% paraffin. The structure of RDX is shown in Figure 1. Cyclohexane and nitrogen dioxide ( $NO_2$ ) may be viewed as the "building blocks" of RDX. Figure 2 shows functional group vibrations in the gas phase spectra of oxides of nitrogen and cyclohexane and the analogous features in the spectrum of solid C-4. Gas phase functional group vibrational frequencies should only be used as a rough guide when interpreting spectra of solid samples, and effects of crystal structure on measured group frequencies (relative to their gas phase counterparts) should not be underestimated. This is important for explosives because vibrations corresponding to movement of the lattice



**Figure 2.** The gas phase infrared absorbance spectrum of cyclohexane ( $C_6H_{12}$ ) and a gas mixture of the simple oxides of nitrogen ( $NO$ ,  $NO_2$ ,  $N_2O$ ), and the infrared photoacoustic spectrum of the solid explosive formulation C-4. (C-4 is made up of approximately 90% RDX and 10% paraffin.) Cyclohexane and nitrogen dioxide ( $NO_2$ ) may be viewed as the "building blocks" of RDX (see Figure 1). There are functional group vibrations in the gas phase infrared spectra of nitrogen dioxide and cyclohexane and the analogous features in the infrared spectrum of solid C-4.

sites in the bulk crystal (phonon modes) may be influential in determining physical properties, such as impact sensitivity. Still, for most explosives studies, group frequencies are used for interpretation of measured vibrational spectra. Table 1 lists some of the group frequencies (values given in  $cm^{-1}$ ) associated with vibrational spectra of explosives.

Vibrational spectroscopic studies of explosives may be grouped roughly into studies of unreacted materials and into studies of products of reaction. Studies of unreacted material often focus on ways in which explosives can be identified, neat and in mixtures, changes that occur over long times and changes in environment, investigations into the structural environment in crystals of neat explosives, pathways of vibrational relaxation following impact, and investigations into thermal and shock induced decomposition mechanisms. Vibrational spectral studies of products of reaction of explosives usually involve heating or some other input of energy, and are almost always focused on understanding the mechanism of decomposition, the kinetics of the decomposition, and the changes in the solid state of the explosive that occur just prior to and in the first stages of chemical reaction. It is worth noting that even though many explosives in use today were first synthesized prior to the Second World War, the exact mechanisms of decomposition and the reasons for differing impact sensitivity in many neat explosives and explosive formulations are not resolved.

#### 5 APPLICATIONS

Most infrared spectra of explosives under static conditions are measured with a Fourier transform infrared (FT-IR)

**Table 1.** Wavenumber ranges and group assignments for spectral features commonly observed ( $600\text{ cm}^{-1}$  to  $3100\text{ cm}^{-1}$ ) in the infrared spectra of explosives.

| Mode assignment                            | Example or type of explosive or EM      | Wavenumber ( $\text{cm}^{-1}$ ) |
|--|---|---------------------------------|
| $\text{NO}_2$ deformation and ring stretch | Nitramine (RDX), TNT                    | 650–850                         |
| Ring torsion                               | Nitramine (RDX), TNT                    | 1000–1080                       |
| N–N stretch                                | Nitramine (RDX)                         | 1200–1230                       |
| $\text{NO}_2$ symmetric stretch            | Nitramine (RDX)                         | 1260–1320                       |
| $\text{CH}_2$ bend                         | Nitramine (RDX), TNT                    | 1300–1450                       |
| $\text{NO}_2$ asymmetric stretch           | Nitramine (RDX), TNT                    | 1450–1600                       |
| C–H stretch                                | Nitramine (RDX), TNT,<br>nitrocellulose | 2900–3100                       |
| N–O stretch                                | Nitrate ester (PETN)                    | 850–950                         |
| C–C stretch                                | TNT                                     | 1620–1700                       |
| $\text{NO}_2$ symmetric stretch            | TNT                                     | 1325–1375                       |
| $\text{NO}_2$ bend                         | Nitrocellulose                          | 800–900                         |
| $\text{NO}_2$ symmetric stretch            | Nitrocellulose                          | 1200–1300                       |
| $\text{NO}_2$ asymmetric stretch           | Nitrocellulose                          | 1600–1700                       |
| C–O stretch                                | Nitrate ester (PETN)                    | 1000–1040                       |

spectrometer. Raman spectra have been measured with both Fourier transform and dispersive spectrometers. Measurements where the sample is not heated or given energy except by the spectroscopic light source itself are described in the next section. Methods that measure the vibrational spectra of the explosive or of reaction products after the explosive is heated or supplied with energy are dealt with in Section 7. After these sections, there is a glossary of the names of different energetic materials and abbreviations for the techniques used to measure and interpret the vibrational spectra of explosives. Finally, we have included in Tables 2–7 a listing of energetic materials by chemical classification, and the methods used in their investigation by vibrational spectroscopy.

## 6 METHODS – NON-THERMAL TECHNIQUES

### 6.1 Transmission FT-IR spectroscopy

Transmission spectroscopy (TS) has been applied to the non-thermal characterization of explosives that were pressed into KBr disks,<sup>12–20</sup> held between/on salt disks,<sup>19,21,22</sup> suspended in Nujol<sup>23</sup> or analyzed in solution.<sup>24,25</sup> Matrix isolation techniques have also been used.<sup>26–28</sup> Analysis of explosives in the vapor phase has been performed using long-pass cells.<sup>29</sup> Films of nitrocellulose have also been analyzed.<sup>30</sup> In general, these studies have focused on comparing measured spectra with calculated spectra, and on measuring changes in explosives and explosive formulations after aging. In Janni *et al.*<sup>29</sup> vapor phase spectra of some molecular explosives (RDX, PETN, TNT) were measured to help determine if infrared techniques could be used for trace detection. As

noted in Janni *et al.*<sup>29</sup> and examined in more detail in Henderson *et al.*,<sup>3</sup> detecting vapor from solid molecular explosives is made even more difficult by the affinity of the vapors to many surfaces.

### 6.2 Attenuated total reflection (ATR)

ATR has been used to study diffusion kinetics of TNT in rubber and adsorption of nitroaromatic compounds on clays.<sup>31,32</sup> An interesting conclusion from this work is that because many explosive molecule vapors have a high affinity for polymeric matrices, trace detection of explosives may give best results when the search for the explosive concentrates on molecules adsorbed onto surfaces, rather than in the vapor phase.

### 6.3 Infrared microscopy

Infrared microscopes have been used to perform depth profiling of solid propellants, primarily for examination of diffusion of plasticizers and deterrents.<sup>33–35</sup> An interesting use of FT-IR microscopy (Mic) applied to propellant formulations is for determining the thickness (tens to hundreds of micrometers) and composition and extent of oxidation of the reaction zone in extinguished propellant grains.<sup>36,37</sup>

### 6.4 FT-IR photoacoustic spectroscopy

FT-IR photoacoustic spectroscopy has been used to characterize a solid propellant formulation with respect to surface vs bulk composition, and thickness of a graphite coating.<sup>38</sup>



Table 2. Ammonium salts.

| Species  | Information or data   | Method <sup>a</sup> | Reference |
|----------|---|---------------------|-----------|
| ADN      | Spectra of "raw" and recrystallized ADN   | TS                  | 18        |
| ADN      | Thermolysis product concentration vs time   | TJ                  | 103       |
| AN       | Spectra of laser ablation products  | TS                  | 136       |
| AN       | Spectra on gold foil  | RAIRS               | 43        |
| AN       | Comment on inability to observe vapor of molecular form   | TS                  | 29        |
| AN       | Thermolysis product concentration vs time   | TJ                  | 103       |
| AN       | Thermolysis product concentration vs time (for AN and AN/EDDN)  | RS                  | 87        |
| AP       | Absorbance and transmittance spectra; refractive index and normal reflection from dispersion theory; absorption coefficient and index                       | TS                  | 15, 16    |
| AP       | Thermolysis product concentration vs time; spectra of gas products  | TJ                  | 105       |
| AP       | Spectra of gas phase thermolysis products for BAMO/NMNO/AP propellants with and without iron oxides   | RS                  | 93        |
| EDDN     | Spectra of gas products; spectra of HNCO and cyanuric acid  | TJ                  | 110       |
| EDDN     | Thermolysis product concentration vs time (for EDDN and EDDN/HN)  | RS                  | 87        |
| FDNPAN   | Spectra, assignments for neat polycrystalline film, polymorphs and melt phase; thermolysis product concentration vs time and pressure                       | RS                  | 82        |
| HAN      | Spectra, assignments for solid, melt; thermolysis product concentration vs time   | RS                  | 68        |
| HAN      | Thermolysis product concentration vs time (for HAN and EDDN/HN)   | RS                  | 87        |
| HAN      | Assignments for thermolysis products  | TS                  | 137       |
| HN       | Thermolysis product concentration vs time (for HN and HAN/HN)   | RS                  | 87        |
| KDN      | Transmission spectra for decomposing KDN; thermolysis product concentration vs time; N <sub>2</sub> O absorption peak at various decomposition temperatures | RS                  | 95        |
| LGP 1845 | Thermolysis product concentration vs time (for HAN, TEAN and LPG 1845)  | RS                  | 85        |
| PTTN     | Spectra of PTTN and thermolysis products; assignments for PTTN  | RS                  | 62        |
| PTTN     | Thermolysis product concentration vs time   | RS                  | 83        |
| PTTP     | Spectrum, assignments   | RS                  | 62        |
| TAGN     | Spectra and table of assignments for neat solid; spectra of neat solid at several temperatures; thermolysis product concentration vs time                   | RS                  | 66        |

<sup>a</sup>TS, transmission spectroscopy; TJ, temperature-jump; RAIRS, reflection-absorption infrared spectroscopy; RS, rapid scan.

The technique is also an excellent tool for measuring spectra of dark and or opaque explosive samples.<sup>39</sup>

### 6.5 Diffuse reflection FT-IR spectroscopy

Diffuse reflection FT-IR spectroscopy has been used to study decomposition of EGDN on zinc oxide, and interfacial bonding in HMX-based propellant.<sup>40,41</sup>

### 6.6 Surface-enhanced infrared and surface-enhanced Raman spectroscopy

These techniques have been used to investigate chemisorption of an azobenzene derivative on silver.<sup>42</sup> They may also hold promise for trace detection of explosives.

### 6.7 Grazing angle reflection/absorption FT-IR spectroscopy

This technique has been used to study ammonium nitrate films on gold.<sup>43</sup>

### 6.8 Theoretical calculations

Ab initio calculations of vibrational spectra have been performed using several different density functional theory codes including: B3LYP and MP2/6-311G\*\*,<sup>26</sup> and HF, BP86, B3P86, and B3LYP for NTO;<sup>27</sup> 94HF/6-31G for TNT;<sup>29</sup> Gaussian 92 for methyl nitrate and derivatives;<sup>44</sup> Gaussian 94, B3LYP/6-311G for di- and trinitromethane and their isotopomers;<sup>45</sup> restricted HF, B3LYP/6-31G\*\* and

Table 3. Azides.

| Species        | Information or data   | Method <sup>a</sup> | Reference |
|----------------|---|---------------------|-----------|
| ADM group      | Assignments for films of four compounds containing the ADM group; spectra of gas thermolysis products       | RS                  | 88        |
| Azobenzene     | FT-IR in KBr; SEIR of monolayers  | SEIR                | 42        |
| BNMO           | Thermolysis product concentration vs time   | RS                  | 74        |
| GAP            | Thermolysis product concentration vs time   | SMATCH              | 99        |
| GAP            | Spectra of products from acoustic shock   | TS                  | 128, 130  |
| GAP            | Thermolysis product concentration vs time. In-depth details of technique                                    | TJ                  | 101       |
| GAP            | Spectra of neat mono-, di-, and tri-ol (liquid and vapor); thermolysis product concentration vs temperature | TJ                  | 112       |
| GAP            | Spectrum and table of assignments for neat monomer and polymer, thermolysis product concentration vs time   | RS                  | 72        |
| GAP            | Thermolysis results compared for 33 EMs   | RS                  | 80        |
| NMMO           | Thermolysis results compared for 33 EMs   | RS                  | 80        |
| NMMO           | Transmission spectrum of oligomer   | TS                  | 13        |
| P-AMMO         | Thermolysis product concentration vs time. Spectra of gas phase products                                    | SMATCH              | 99        |
| P-AMMO         | Thermolysis product concentration vs time. In-depth details of technique                                    | TJ                  | 101       |
| P-AMMO         | Spectra, assignments for monomer, polymer; thermolysis product concentration vs time                        | RS                  | 72        |
| P-AMMO         | Thermolysis product concentration vs pressure; thermolysis results compared for 33 EMs                      | RS                  | 80        |
| P-AZOX         | Spectra, assignments for monomer, polymer; thermolysis product concentration vs time                        | RS                  | 72        |
| P-BAMO         | Spectra, assignments for monomer, polymer; thermolysis product concentration vs time                        | RS                  | 72        |
| P-BAMO         | Thermolysis product concentration vs time   | SMATCH              | 99        |
| P-BAMO         | Thermolysis product concentration vs time. In-depth details of T-Jump technique                             | TJ                  | 101       |
| P-BAMO         | Thermolysis product concentration vs time   | RS                  | 74        |
| P-BAMO         | Thermolysis results compared for 33 EMs   | RS                  | 80        |
| P-BAMO/BNMO    | Spectra of gas phase thermolysis products for P-BAMO/BNMO   | RS                  | 74        |
| P-BAMO/NMMO/AP | Spectra of gas phase thermolysis products for BAMO/NMMO/AP propellants with and without iron oxides         | RS                  | 93        |
| P-DAPMMO       | Spectra, assignments for monomer, polymer; thermolysis results compared for 33 EMs                          | RS                  | 72        |
| P-DAPMO        | Thermolysis results compared for 33 EMs   | RS                  | 80        |
| P-NMMO         | Thermolysis product concentration vs time   | SMATCH              | 97        |
| P-NMMO         | Thermolysis product concentration vs time   | RS                  | 74        |
| P-NMMO         | Thermolysis results compared for 33 EMs   | RS                  | 80        |

<sup>a</sup>SEIR, surface-enhanced infrared; SMATCH, simultaneous mass and temperature change.

BP86/6-31G\*\* for DNAZ and derivatives,<sup>28</sup> MP2/6-31G\* for tetrazole and derivatives.<sup>46</sup> Semi-empirical calculations for TNT can be found in Wadwani *et al.*<sup>23</sup> These studies are often accompanied by FT-IR transmission spectra of the explosive molecule of interest (see Section 6.1).

## 6.9 Raman spectroscopy

Raman spectroscopy has been shown to be a valuable technique for the characterization of many explosives and explosive formulations, especially those containing molecular crystals (e.g. RDX).<sup>47-52</sup> Reasonably good

spectra of neat polymeric samples (e.g. NC) may also be obtained. However, Raman spectroscopy may be of limited use for many colored formulations of polymeric energetic materials (NC containing formulations are often colored, e.g. JA2, M9, M30, which range in color from dull yellow to almost black) and for other darkly colored samples (even very yellow crystals of slightly impure TNT) because these samples tend to absorb the scattering radiation and decompose or heat up to an extent that the Raman signal is overwhelmed by a thermal signature. Because Raman linewidths are more narrow than those measured using absorption based measurements, it is possible to see slight impurities in samples and in mixtures of many explosive

Table 4. Nitramines.

| Species              | Information or data  | Method <sup>a</sup> | Reference |
|----------------------|--|---------------------|-----------|
| DATH                 | Spectra of solid, melt, acetone solution, and thermolysis products; assignments for neat solid                               | RS                  | 77        |
| DATH                 | Thermolysis product concentration vs time  | RS                  | 83        |
| DMEDNA               | Thermolysis product concentration vs time  | RS                  | 79        |
| DMHDNA               | Thermolysis product concentration vs pressure  | RS                  | 79        |
| DNAZ                 | Calculated and experimental spectra  | TS                  | 28        |
| DNAZ-DN              | Spectra, tables of assignments, phase diagram  | DAC                 | 124       |
| DNCP                 | Thermolysis product concentration vs time  | RS                  | 76        |
| DNCP                 | Thermolysis results compared for 33 EMs  | RS                  | 80        |
| DNFP                 | Thermal data confirming infrared data from Oyumi <i>et al.</i> <sup>75</sup> and Oyumi and Brill <sup>80</sup>               | RS                  | 81        |
| DNFP                 | Comments on infrared results; mostly thermal data  | RS                  | 92        |
| DNFP                 | Spectra, assignments for four polymorphs, melt; thermo product concentration vs time   | RS                  | 75        |
| DNFP                 | Thermolysis results compared for 33 EMs  | RS                  | 80        |
| DNNC                 | Spectra, tables of assignments for solid, melt, aerosol  | TS                  | 21        |
| DNNC                 | Thermolysis product concentration vs time  | SMATCH              | 100       |
| DNNC                 | Thermolysis product concentration vs time  | RS                  | 64        |
| DNP                  | Thermolysis product concentration vs time  | RS                  | 79        |
| DPT                  | Thermolysis results compared for 33 EMs  | RS                  | 80        |
| EDN, metal complexes | Spectra of copper salt below/above decomposition temperature; thermolysis product concentration vs time                      | RS                  | 86        |
| EDN, metal complexes | Comments on trends between $\angle_{as}(\text{NO}_2)$ and N-N bond distances and coordination modes of the nitramine ligands | TS                  | 22        |
| EDNA                 | Thermolysis product concentration vs time and pressure   | RS                  | 79        |
| EDNA                 | Thermolysis results compared for 33 EMs  | RS                  | 80        |
| HMX                  | Assignments for thermolysis products   | T                   | 137       |
| HMX                  | Chemical shift for DR bands, interface study   | DR                  | 41        |
| HMX                  | Spectra; refractive index and normal reflection from dispersion theory; absorption coefficient and index                     | TS                  | 16, 20    |
| HMX                  | Thermolysis product concentration vs time; in-depth details of T-Jump technique  | TJ                  | 101       |
| HMX                  | Thermolysis product concentration vs time  | TJ                  | 106       |
| HMX                  | Spectra of solid as function of temperature; spectra of gas phase thermo products  | RS                  | 61        |
| HMX                  | Thermolysis product concentration vs time  | RS                  | 73        |
| HMX                  | Spectra for four polymorphs; thermolysis product concentration vs pressure   | RS                  | 78        |
| HMX                  | Thermolysis results compared for 33 EMs  | RS                  | 80        |
| HMX                  | Thermolysis product concentration vs time (thin film samples)  | RS                  | 91        |
| HNDZ                 | Spectra, tables of assignments for solid at 25°C   | TS                  | 21        |
| HNDZ                 | Thermolysis product concentration vs time  | RS                  | 64        |
| HNDZ                 | Thermolysis results compared for 33 EMs  | RS                  | 80        |
| HNIW                 | Spectra, tables of assignments for $\alpha$ -, $\beta$ -, $\epsilon$ -, $\zeta$ -HNIW  | DAC                 | 121       |
| HNIW                 | Spectra of HNIW polymorphs, phase diagram  | DAC                 | 122       |
| HNIW                 | Spectra, assignments for HNIW in DAC/GAC, residue, products  | GAC                 | 123       |
| HNIW                 | Thermolysis product concentration vs time; spectrum of HNIW  | TJ                  | 102       |
| HNIW                 | Residue thermolysis products concentration vs time   | TJ                  | 104       |
| MBNA                 | Thermolysis product concentration vs pressure  | RS                  | 79        |
| MEDINA               | Thermolysis product concentration vs time and pressure   | RS                  | 79        |
| MEDINA               | Gas phase thermolysis results compared for 33 EMs  | RS                  | 80        |
| MN, metal complexes  | Comments on trends between $\angle_{as}(\text{NO}_2)$ and N-N bond distances and coordination modes of the nitramine ligands | TS                  | 22        |
| MN, metal complexes  | Thermolysis product concentration vs time  | RS                  | 86        |
| MRDX                 | Spectra, assignment for neat solid/melt; thermolysis product concentration vs time   | RS                  | 65        |
| NAT, metal complexes | Comments on trends between $\angle_{as}(\text{NO}_2)$ and N-N bond distances and coordination modes of the nitramine ligands | TS                  | 22        |

(Continued overleaf)

Table 4. (continued)

| Species              | Information or data  | Method <sup>a</sup> | Reference |
|----------------------|--|---------------------|-----------|
| NAT, metal complexes | Thermolysis product concentration vs time  | RS                  | 86        |
| N-DNAZ               | Calculated and experimental spectra  | TS                  | 28        |
| OHEX                 | Spectra, tables of assignments for four polymorphs, melt phase; thermolysis product concentration vs pressure  | RS                  | 78        |
| OHEX                 | Thermolysis results compared for 33 EMs  | RS                  | 80        |
| ONDO                 | Spectra, assignments for neat solid; thermolysis product concentration vs time   | RS                  | 67        |
| PNDNBs               | Spectra, assignments for neat solids; thermolysis product concentration vs time  | RS                  | 70        |
| PNFTOs               | Spectra, assignments for five polymorphs of TNDBN, TNDBN(V) in acetone-d <sub>6</sub> , and two polymorphs of DPT; thermolysis product concentration vs time | RS                  | 69        |
| RDX                  | Spectra of thin film laser thermolysis products  | TS                  | 126       |
| RDX                  | Spectra of thin film laser thermolysis products  | TS                  | 127       |
| RDX                  | Assignments for thermolysis products   | TS                  | 137       |
| RDX                  | Spectra of polymorphs of RDX as a function of temperature and pressure   | DAC                 | 120       |
| RDX                  | Spectra of vapor and decomposition products  | TS                  | 29        |
| RDX                  | Absorbance spectra; refractive index and normal reflection from dispersion theory; absorption coefficient and index  | TS                  | 16, 20    |
| RDX                  | Thermolysis product concentration vs time  | TJ                  | 109       |
| RDX                  | Thermolysis product concentration vs temperature; spectra of gas products.   | TJ                  | 114       |
| RDX                  | Spectra of solid as function of temperature; spectra of gas phase thermolysis products   | RS                  | 61        |
| RDX                  | Spectra, assignments for gas phase thermolysis products; thermolysis product concentration vs time   | RS                  | 63        |
| RDX                  | Thermolysis product concentration vs pressure; comparison of results   | RS                  | 80        |
| TNDBN                | Thermolysis results compared for 33 EMs  | RS                  | 80        |
| TNSD                 | Thermolysis product concentration vs time  | RS                  | 76        |
| TNSD                 | Thermolysis results compared for 33 EMs  | RS                  | 80        |
| TNSU                 | Thermolysis product concentration vs time  | RS                  | 76        |
| TNSU                 | Thermolysis results compared for 33 EMs  | RS                  | 80        |
| TNTO                 | Thermolysis product concentration vs pressure; results compared with 33 other EMs  | RS                  | 80        |
| TRDX                 | Spectra, assignment for neat solid, spectrum of "premelt"; thermolysis product concentration vs time   | RS                  | 65        |

<sup>a</sup>DAC, diamond anvil cell; DR, diffuse reflection.

materials. Figure 3 shows the slight impurity of HMX often found in RDX manufactured in the US, relative to that of pure RDX.<sup>53</sup> The well resolved spectra may have forensic uses. An interesting application of this is the use of Raman spectra with neural networks to develop screening techniques to determine whether or not an unknown compound is energetic.<sup>54-60</sup>

## 7 METHODS – THERMAL TECHNIQUES

### 7.1 Rapid-scan FT-IR spectroscopy

Rapid-scan FT-IR spectroscopy is the basis of many investigations of the thermal decomposition of explosives.<sup>61-95</sup>

We use the term "rapid scan" somewhat loosely, but in general we mean FT-IR spectra recorded in scan times less than 250 ms, with no co-adding, so each spectrum is measured over the smallest possible time interval. Probably the most well known applications of rapid-scan FT-IR spectroscopy as applied to explosives are the two techniques developed by Brill *et al.* These are SMATCH (Simultaneous mass and temperature change)/FT-IR spectroscopy<sup>96-100</sup> and T (Temperature)-Jump FT-IR<sup>101-118</sup> spectroscopy, which both rely on rapid scanning of the FT-IR spectrometer to obtain real-time spectra of thermolysis products. For SMATCH/FT-IR experiments, a sample of the energetic material is placed on a heatable quartz oscillator/stainless steel sample holder, which is contained in an infrared transmission cell. Mass change during heating is monitored

Table 5. Nitrates.

| Species              | Information or data   | Method <sup>a</sup> | Reference |
|----------------------|---|---------------------|-----------|
| EGDN                 | Spectra of EGDN and gas phase decomposition products  | DR                  | 40        |
| GN oligomer          | Transmission spectrum   | TS                  | 13, 14    |
| HNMB                 | Thermolysis product concentration vs time   | RS                  | 74        |
| Methyl nitrate       | Calculated spectra for methyl nitrate and five of its derivatives                               | Theory              | 44        |
| N5 propellant        | Refractive index and normal reflection from dispersion theory; absorption coefficient and index | TS                  | 16        |
| NaNO <sub>3</sub>    | Spectra of combustion products (NaNO <sub>3</sub> /C/S)   | ES                  | 136       |
| NC                   | Spectra and tables of assignments for irradiated and neat NC                                    | TS                  | 134       |
| NC                   | Spectra of NC at 151 °C as a function of time   | TS                  | 131       |
| NC                   | Spectrum between 5.8–6.05 $\mu$ m, quantitative method  | TS                  | 24        |
| NC                   | Transmission spectra of NC/polyurethane films   | TS                  | 30        |
| NC                   | Thermolysis product concentration vs time. Details of SMATCH/FT-IR technique                    | SMATCH              | 96, 97    |
| NC                   | Thermolysis product concentration vs time   | RS                  | 74        |
| NC                   | Thermolysis results compared for 33 EMs   | RS                  | 80        |
| NC                   | Spectra of gas phase decomposition products   | RS                  | 94        |
| NC propellant        | Depth profiling of propellant; looking for stabilizer and deterrent                             | Mic                 | 34        |
| NC propellant        | Depth profiling of propellant; looking for stabilizer and deterrent                             | Mic                 | 35        |
| PETN                 | Spectra of PETN at 162 °C as a function of time, gas products, residue                          | TS                  | 132       |
| PETN                 | Spectra of vapor and decomposition products   | TS                  | 29        |
| PETN                 | Thermolysis product concentration vs time   | RS                  | 74        |
| PETN                 | Thermolysis results compared for 33 EMs   | RS                  | 80        |
| PETN-NF <sub>2</sub> | Spectra of neat material, thermolysis products, residue (with/without B)                        | GAC                 | 125       |
| PGN                  | Thermolysis product concentration vs time   | SMATCH              | 97        |
| PVN                  | Thermolysis product concentration vs time   | SMATCH              | 97        |
| TEGDN                | Thermolysis product concentration vs time   | RS                  | 74        |
| TEGDN                | Thermolysis results compared for 33 EMs   | RS                  | 80        |
| TNM                  | Table of assignments for gas phase  | TS                  | 45        |

<sup>a</sup>ES, emission spectroscopy; Mic, Microscopy; GAC, gem anvil cell.

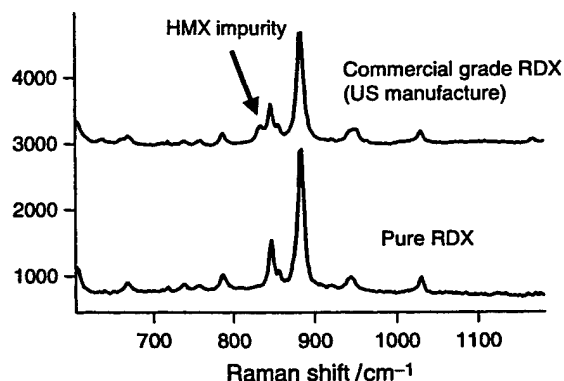


Figure 3. Raman spectrum showing the slight impurity of HMX often found in RDX manufactured in the US, relative to that of pure RDX.

by measuring the change in the resonant frequency of the quartz oscillator which holds the sample, and chemical change is monitored by measuring the infrared spectrum of gases produced during heating. SMATCH/FT-IR

spectroscopy is a sampling technique useful for studying the rapid thermolysis of explosives and provides sample mass, relative composition of gas decomposition products, and temperature change as a function of time. Heating rates are limited by the quartz oscillator/stainless steel sample holder used to determine mass loss, but are sufficiently high ( $>300^{\circ}\text{C/s}^{-1}$ ) that data may be used to determine kinetics and chemical mechanisms of thermal decomposition for many energetic materials.

T-Jump/FT-IR spectroscopy<sup>101–118</sup> was designed to elucidate some of the microscopic details of the very rapid thermal decomposition mechanism of solids and liquids. The experimental apparatus is the interface of a modified, commercial, filament pyrolysis control unit and an FT-IR spectrometer. In T-Jump/FT-IR spectroscopy, a Pt ribbon filament is used to heat a thin film of material at a very fast rate ( $2000^{\circ}\text{C/s}^{-1}$ ), resulting in conditions that for an explosive material mimic the surface under ignition conditions. The Pt ribbon filament serves as both the heat source and the sensor of temperature and thermochemical changes of the

Table 6. Nitros.

| Species                     | Information or data   | Method <sup>a</sup> | Reference |
|-----------------------------|---|---------------------|-----------|
| ANTA                        | Spectrum of thermolysis residue; thermolysis product concentration vs pressure  | TS                  | 12        |
| ANTA                        | Calculated spectra for all tautomers  | Theory              | 145       |
| Dinitro-methane             | Calculated spectra for gas and isotopomer   | Theory              | 45        |
| Nitro furazans              | Spectra and/or discussion of gas phase thermolysis products for six energetic furazan compounds   | TJ                  | 113       |
| Nitro furoxans              | Assignments for five neat nitro benzofuran solids; spectra of residue from one and gas products of another; thermolysis product concentration vs time | RS                  | 73        |
| Nitromethyl-1,3,5-triazines | Summary of spectra of three derivatives   | TS                  | 17        |
| NTO                         | Spectrum of thermolysis residue; thermolysis product concentration vs pressure  | TS                  | 12        |
| NTO                         | Calculated and experimental spectra   | TS                  | 26        |
| NTO                         | Product identities used to verify when sublimation or decomposition was dominant process on thermal treatment   | TJ                  | 108       |
| NTO                         | Spectra of products from acoustic shock   | TS                  | 129       |
| NTO, metal salts of         | Thermolysis product spectra, concentration vs time; Na, Li, K, Cu, Cs, Pb salts   | TJ                  | 115       |
| NTPs                        | Experimental (transmission) and calculated spectra for labeled and unlabeled 6-NTP; study of tetrazole-azide tautomerism                              | TS                  | 25        |
| PA, metal salts of          | Thermolysis product spectra, concentration vs time; K, Cs, and Pb salts   | TJ                  | 115       |
| PNC, PNCA                   | Spectra, assignments for neat TNBA, DNVA, BTNC, BDNC; spectra of neat solids at several temperatures; thermolysis product concentration vs time       | RS                  | 71        |
| TATB                        | Thermolysis product concentration vs time. In-depth details of T-Jump technique   | TJ                  | 101       |
| TNAZ                        | Spectra, tables of assignments at 25 °C   | TS                  | 21        |
| TNAZ                        | Calculated, experimental spectra for TNAZ and labeled TNAZ  | TS                  | 27        |
| TNAZ                        | Thermolysis product concentration vs time   | RS                  | 64        |
| TNAZ                        | Thermolysis results compared for 33 EMs   | RS                  | 80        |
| TNB                         | Spectra of TNB on clays   | ATR                 | 32        |
| TNDPTP                      | List of frequencies for 11 derivatives  | TS                  | 19        |
| TNT                         | Spectra of TNT at 209 °C as function of time, gas products, residue   | TS                  | 132       |
| TNT                         | Spectra of TNT diffusing into rubber  | ATR                 | 31        |
| TNT                         | Spectra, assignments at 25 °C; calculated values  | TS                  | 23        |
| TNT                         | Spectra of vapor and decomposition products   | TS                  | 29        |
| Trinitromethane             | Calculated spectra for liquid and isotopomer  | Theory              | 45        |

<sup>a</sup>ATR, attenuated total reflection.

sample. Measuring transmission through gases immediately above the sample, a RS FT-IR spectrometer is synchronized to the Pt ribbon heating pulse, and the temporal evolution of gases produced by the sample is measured. For many energetic materials, T-Jump/FT-IR spectroscopy provides sufficient control over the heating conditions to allow mechanistic detail to be obtained about the chemistry of the condensed phase during simulated combustion and explosion. The output of the experiment is a simultaneous trace of thermal response of the condensed heterophase layer and the FT-IR spectra of the near-surface gas products. Figure 4 shows the structure and T-Jump/FT-IR data for the organoazide polymer AMMO. The difference control

voltage (the voltage change required to compensate for heat added to or removed from the filament by the sample) shows an initial endotherm corresponding to onset of melting in the sample. The endotherm gradually decreases as the AMMO melts. At about 4 s after the heating pulse, exothermic reaction begins, liberating N<sub>2</sub> (not infrared active), and several gaseous products (Figure 4). By measuring the temperature dependence of the HCN/NH<sub>3</sub> ratio, it was shown for AMMO that C-N bond retention is favored at higher temperature.<sup>101</sup> More recently, infrared inactive gases have been measured using T-jump/FT-Raman spectroscopy.<sup>118</sup>

An interesting example of the T-jump technique applied to molecular crystalline energetic materials involves the

Table 7. Non-nitramine/nitrate/nitro/azide.

| Species                     | Information or data  | Method | Reference |
|-----------------------------|--|--------|-----------|
| ATRZ, 3-                    | Spectrum of thermolysis residue; thermolysis product concentration vs pressure   | T      | 12        |
| ATRZ, 4-                    | Spectrum of thermolysis residue; thermolysis product concentration vs pressure   | T      | 12        |
| ATZ, 1-                     | Thermolysis product concentration vs time  | RS     | 90        |
| ATZ, 5-                     | Spectra of solid anhydrous ATZ, gas phase thermolysis products; spectra of gas products for Cl, Br, and I salts  | TJ     | 116       |
| ATZ, 5-                     | Spectra of thermolysis gas products; thermolysis product concentration vs time   | RS     | 90        |
| AZ                          | Calculated and experimental spectra  | T      | 28        |
| BP                          | Spectra of BP and gas phase thermolysis products as function of time   | TJ     | 111       |
| DATZ, 1,5-                  | Spectra of thermolysis gas products; thermolysis product concentration vs time   | RS     | 90        |
| DATZ, 2,5-                  | Spectra of thermolysis gas products; thermolysis product concentration vs time   | RS     | 90        |
| DTRZ, 3,5-                  | Spectrum of thermolysis residue; thermolysis product concentration vs time   | T      | 12        |
| HNF                         | Thermolysis product concentration vs time; spectra of gas products   | TJ     | 106       |
| HNF                         | Spectrum and assignments for dry, solid HNF, and spectrum of gas products; thermolysis product concentration vs time   | TJ     | 107       |
| HTPB                        | Absorbance and transmittance spectra; absorption coefficient and index   | T      | 15, 16    |
| HTPB                        | Spectra of thermolysis residue and gas products  | SMATCH | 98        |
| IPDI-HTPB                   | Spectra of thermolysis residue and gas products  | SMATCH | 98        |
| Propiolates, metal salts of | Spectra of neat Na, K, and Rb salts; spectra of thermolysis gas products for same; spectra of decomposing "dry" K salt; spectra of residues from K, Rb, and Zn salts | RS     | 89        |
| PSP                         | Spectra of PSP and gas phase thermolysis products as function of time  | TJ     | 111       |
| Tetrazoles                  | Assignments for calculated spectra for seven hydroxyl derivatives  | Theory | 46        |

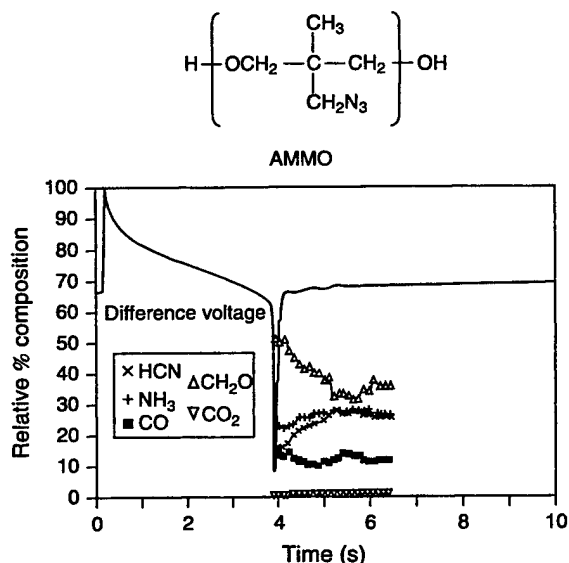
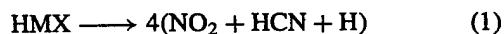


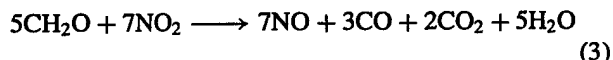
Figure 4. The chemical structure of the organoazide polymer AMMO and T-Jump/FT-IR data for 200  $\mu\text{g}$  of AMMO heated at 2000  $^{\circ}\text{C}/\text{s}^{-1}$  to a final temperature of 306  $^{\circ}\text{C}$  under 2.7 atm pressure of Ar. [Reproduced by permission from Brill *et al.* (1992).<sup>101</sup>]

investigation of the decomposition of RDX ( $\text{C}_3\text{H}_6\text{N}_6\text{O}_6$ ) and its eight member homolog HMX ( $\text{C}_4\text{H}_8\text{N}_8\text{O}_8$ ). In one of the more well known papers on explosive material decomposition (using molecular beam mass spectrometry), Zhao *et al.*<sup>119</sup> showed that gas phase laser induced

decomposition of the RDX molecule (see Figure 1) may occur via competing pathways involving N–N bond scission or “depolymerization” creating the methylene nitramine radical ( $\text{CH}_2\text{NNO}_2$ ). The T-jump FT-IR technique was used to investigate whether these pathways compete during solid phase thermal decomposition, or whether other mechanisms are involved. Brill *et al.*<sup>101</sup> concluded that for HMX, heating of the solid results in an initial thermoneutral decomposition which follows two pathways:



As temperature is increased, equation (1) becomes more important. Energy is liberated during the process when the products of reactions (1) and (2) react:



A further sophistication of the T-Jump technique has been developed by Kim *et al.*<sup>117</sup> This technique, referred to as confined rapid thermolysis FT-IR spectroscopy, does not allow gases evolved during heating to pass into a low temperature region prior to being measured. Solid samples are confined within two closely spaced isothermal surfaces, and the spectra of the confined gases are measured in situ. An additional advantage of this technique is that it can be used for samples that might readily vaporize, have the tendency to stick to a heated surface, or are catalytically

affected by the nichrome or Pt filaments often used in other thermolysis techniques. RS FT-IR techniques have also been used to characterize in-situ changes in condensed phase material as a function of time, as for example in the progression of a solid explosive (RDX and HMX) through its melting point and decomposition.<sup>61</sup>

Rapid scan techniques have also been applied to the investigation of the thermolysis of the following materials: AMMO, AN, ATZ, AZOX, BAMO, BTTN, DAPMMO, DATHDNFP, DATZ, DMEDNA, DNNC, EDDN, EDNA, GAP, HAN, HMX, HNDC, KDN, MBNA, MEDINA, NC, OHMX, ONDO, PETN, PTTN, RDX, TAGN, TEAN, TEGDN, TMETN, TNAZ, and TNDBN. SMATCH/FT-IR has been applied to the investigation of the thermolysis of the following explosive and/or energetic materials: AMMO, BAMO, DNNC, GAP, NC, NMMO, PGN, PVN, and TNDA. It has also been applied to HPTB, which is not energetic, but is a common rocket propellant ingredient and is therefore included here. T-Jump/FT-IR has been applied to the investigation of the thermolysis of the following explosive and/or energetic materials: AMMO, ADN, AN, AP, BAMO, BP, EDDN, GAP, HMX, HNF, HNIW, HNIW residue, NTO, PA, PDDN, PSP, RDX, and TATB. Confined rapid thermolysis FT-IR spectroscopy has been used to study the decomposition of HAN, HMX, and RDX.

## 7.2 DAC/GAC – microspectroscopy

DACs or GACs are used for the determination of decomposition kinetics as well as chemical reactivity and phase behavior of explosives.<sup>120–125</sup> DAC studies have been performed on DNAZ-DN, HNIW, PETN-NF2 and RDX.

## 7.3 Transmission FT-IR spectroscopy of thin films

Traditional transmission FT-IR spectroscopy has been performed on vapor-deposited thin films of explosives by Wight *et al.* to determine chemical mechanisms of shock- or laser-induced decomposition.<sup>126–130</sup> This technique has been used to examine the decomposition of GAP, NTO, and RDX. This experimental arrangement is complementary to T-Jump/FT-IR spectroscopy in that it examines the gas phase decomposition products of explosive materials after exposure to a short pulse of infrared laser radiation (e.g. 35  $\mu$ s pulse at a wavelength of 10  $\mu$ m), achieving heating rates higher than those obtained using RS thermolysis techniques. Using this technique, Wight *et al.* found evidence of N–N bond scission as the initial decomposition step in the onset of rapid thermolysis in RDX. No evidence of the formation of methylenenitramine was found.

## 7.4 High temperature FT-IR spectroscopy

In a technique developed by Makashir *et al.*, a brass furnace is used to heat an explosive sample which has been pressed into a KBr disk.<sup>131–133</sup> The output of the experiment is a series of spectra as a function of time (on the order of minutes). The thermal decomposition of NC, PETN, and TNT has been studied by this method.

## 7.5 Low temperature FT-IR

Merhari *et al.*<sup>134</sup> have frozen (110 K) substrates and coated them with nitrocellulose under vacuum and then exposed this sample to ionizing radiation. Spectra are obtained as a function of time, and as the sample and substrate are allowed to warm. Pasternack and Rice<sup>135</sup> have used matrix isolation to trap laser ablation products of ammonium nitrate.

## 7.6 Emission FT-IR spectroscopy

Hussain and Rees<sup>136</sup> have used emission FT-IR spectroscopy to study the decomposition of sodium nitrate in a black powder substitute. The sample is pressed into a pellet and ignited. Single beam emission spectra are collected as a function of time.

## 7.7 Raman spectroscopy

A few investigations have used FT-Raman spectroscopy to investigate changes in the solid state of explosives and explosive formulations as decomposition temperature is approached. Fell *et al.*<sup>138</sup> found that Raman spectra of RDX decreased in intensity as the melting point of the material was approached. Raman spectroscopy has also been applied to the investigation of the mechanism of shock induced chemistry in the solid phase. A controversy exists regarding the mechanism of shock and/or impact initiation in explosive materials. Kunz has proposed a solid state interpretation whereby impact causes a change in the energy gap between the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) in explosive materials, and promotion of an electron across this gap (so-called impact induced “metallization”) results in the initial stages of decomposition.<sup>139</sup> Coffey believes that impact/shock initiation results from plastic flow within the explosive material, and the initiation is caused by friction at imperfections (“hot spots”) in the lattice.<sup>140</sup> Others have put forward the idea of vibrational up-pumping as contributing to impact/shock initiation.<sup>141–143</sup> In this theory,



initial energy from shock/impact is deposited into the bulk explosive material via the phonon modes. The efficiency of energy transfer from the "bath" of phonon modes to localized, internal vibrational modes of the molecules at the lattice sites determines the degree to which an explosive is shock/impact sensitive. To investigate this theory, since the energy transfer is extremely rapid (pico- to femtosecond regimes), vibrational energy transfer is monitored by time resolved Raman spectroscopy immediately following a shock wave (usually laser generated) passing through the material.<sup>141</sup> The scattered laser energy may be collected using a time gated camera, or using a streak camera, synchronized to the laser used to produce the shock wave.

## 8 CONCLUSION

Vibrational spectroscopy continues to be a useful tool for the characterization of explosives and other energetic materials, for forensic applications, and for investigations of the ways in which these materials liberate energy. Advances in computational methods<sup>144,145</sup> enabling accurate calculation of vibrational spectra of many solid and liquid materials will increase the number of applications of vibrational spectroscopy to the study of energetic materials. Additionally, advances in signal processing, processor speeds, solid state light sources, modulation techniques, and detectors will enable spectra to be measured more rapidly and in more challenging environments for investigations of the next generation of energetic materials.

## ACKNOWLEDGMENTS

The authors would like to thank Dr Pamela Kaste for suggestions for improvement of this manuscript, and for assistance in measuring the spectra of some explosive formulations.

## ABBREVIATIONS AND ACRONYMS

|        |  |
|--------|--|
| DAC    | Diamond Anvil Cell                       |
| DR     | Diffuse Reflection                       |
| ES     | Emission Spectroscopy                    |
| GAC    | Gem Anvil Cell                           |
| HOMO   | Highest Occupied Molecular Orbital       |
| LUMO   | Lowest Unoccupied Molecular Orbital      |
| Mic    | Microscopy                               |
| RS     | Rapid Scan                               |
| SEIR   | Surface-enhanced Infrared                |
| SMATCH | Simultaneous Mass and Temperature Change |
| TJ     | Temperature-jump                         |
| TS     | Transmission Spectroscopy                |

## LIST OF SYMBOLS

|           |   |
|-----------|---|
| ADM group | Azidodimethyl group   |
| AMMO      | Azidomethylmethyl oxetane                                     |
| AN        | Ammonium nitrate  |
| AND       | Ammonium dinitramide  |
| ANTA      | 3-Amino-5-nitro-1,2,4-triazole                                |
| AP        | Ammonium perchlorate  |
| ATR       | Attenuated total reflection                                   |
| ATRZ      | 3 (or 4)-Amino-1-hydrogen-1,2,4-triazole                      |
| ATZ       | Aminotetrazole  |
| AZ        | Azetidine   |
| AZOX      | Azidooxetane  |
| B         | Boron   |
| BAMO      | Bis(azidomethyl)oxetane                                       |
| BDNC      | Bis(2,2-dinitropropyl)carbonate                               |
| BNMO      | Bis(nitrato)methyloxetane                                     |
| BP        | Benzoyl peroxide  |
| BTNC      | Bis(2,2,2-trinitroethyl)carbonate                             |
| BTTN      | 1,2,4-Butanetriol trinitrate                                  |
| C         | Carbon  |
| CAB       | Cellulose acetate butyrate                                    |
| CRT       | Confined rapid thermolysis                                    |
| DAC       | Diamond anvil cell  |
| DAPMMO    | Diazidopropoxymethyl methyl oxetane                           |
| DATH      | 1,7-Diazido-2,4,6-trinitro-2,4,6-triazaheptane                |
| DATZ      | Diaminotetrazole  |
| DEP       | Diethyl phthalate   |
| DMEDNA    | <i>N,N'</i> -dimethyl- <i>N,N'</i> -dinitro-1,2-ethanediamine |
| DMHDNA    | <i>N,N'</i> -dimethyl- <i>N,N'</i> -dinitro-1,6-hexanediamine |
| DNAZ      | 3,3-Dinitroazetidine  |
| DNAZ-DN   | Dinitro azetidium dinitramide                                 |
| DNCP      | 1,3-Dinitroimidazoleidine                                     |
| DNFP      | 1,4-Dinitrofurazano[3,4- <i>b</i> ]piperazine                 |
| DNNC      | 1,3,5,5-Tetranitrohexahydropyrimidine (or TNDA)               |
| DNP       | <i>N,N'</i> -dinitropiperazine                                |
| DNVA      | 3,3-Dinitrovaleric acid                                       |
| DPT       | 3,7-Dinitro-1,3,5,7-tetrazabicyclo[3.3.1]nonane               |
| DTRZ      | 3,5-Diamino-1-hydrogen-1,2,4-triazole                         |
| EDDN      | Ethylenediammonium dinitrate                                  |
| EDN       | Ethylenedinitramine   |
| EDNA      | <i>N,N'</i> -dinitro-1,2-ethanediamine                        |
| EGDN      | Ethyleneglycol dinitrate                                      |
| EM        | Energetic material  |

|               |  |                      |   |
|---------------|--|----------------------|---|
| FDNPAN        | Fluorodinitropropylammonium nitrate                                | PETN                 | Pentaerythritol tetranitrate  |
| GAP           | Glycide azide polymer  | PETN-NF <sub>2</sub> | PETN-difluoramine   |
| GN            | Glycidyl nitrate   | P-GN                 | Poly glycidyl nitrate   |
| HAN           | Hydroxylammonium nitrate   | PNC                  | Polynitroaliphatic carbonates   |
| HMX           | Octahydro-1,3,5,7-tetrocine  | PNCA                 | Polynitroaliphatic carboxylic acids   |
| HN            | Hydrazinium nitrate  | PNDBN                | Polynitro-3,7-diazabicyclo-[3.3.1]nonane  |
| HNDZ          | 1,3,3,5,7,7-Hexanitro-1,5-diazacyclooctane                         | PNFTO                | Polynitro-3,3,7,7-tetrakis-(trifluoromethyl)-2,4,6,8-tetraazabicyclo[3.3.0]octane   |
| HNF           | Hydrazinium nitroformate   | P-NMMO               | Poly-NMMO   |
| HNIW          | Hexanitrohexaazaisowurtzitane                                      | PSP                  | Poly(styrene peroxide)  |
| HNMB          | Hexanitratomethylbenzene   | PTTN                 | Pentaerythrityltetraammonium nitrate  |
| HTPB          | Hydroxy terminated polybutadiene (non energetic propellant binder) | PTTP                 | Pentaerythrityltetraammonium perchlorate  |
| IPDI-HTPB     | Isophoronediiisocyanate  | PVN                  | Polyvinylnitrate  |
| JA2           | NC (60%), NG (15%), DEGDN (25%)                                    | RDX                  | Hexahydro-1,3,5-trinitro- <i>s</i> -triazine  |
| KBr           | Potassium bromide  | TAGN                 | Triaminoguanidinium nitrate   |
| KDN           | Potassium dinitramide  | TATB                 | Triaminotrinrobenzene   |
| LGP 1845      | Liquid gun propellant (HAN/TEAN/water)                             | TEGDN                | Triethylene glycol dinitrate  |
| LOVA          | Low vulnerability ammunition (RDX, NC, CAB, plasticizer)           | THF                  | Tetrahydrofuran   |
| M9            | NC (60%), NG (40%)   | TMETN                | Trimethylolethane trinitrate  |
| M30           | NQ (50%), NC (30%), NG (15%)                                       | TNAD (c-1,3,5,7)     | <i>cis</i> -(±)-Decahydro-1,3,5,7-tetranitropyrimidino[5.4- <i>d</i> ]pyrimidine    |
| M43           | RDX (76%)  | TNAD (t-1,3,5,7)     | <i>trans</i> -(±)-Decahydro-1,3,5,7-tetranitropyrimidino[5.4- <i>d</i> ]pyrimidine  |
| MBNA          | <i>N</i> -methyl- <i>N</i> -nitro-1-butanamine                     | TNAD (t-1,4,5,8)     | <i>trans</i> -Decahydro-1,4,5,8-tetranitropyrzino[2.3- <i>b</i> ]pyrazine           |
| MEDINA        | <i>N,N'</i> -dinitromethanediamine                                 | TNAZ                 | 1,3,3-Trinitroazetidine   |
| MN            | Methylnitramine  | TNB                  | Trinitrobenzene   |
| MRDX          | Hexahydro-1,3-dinitroso- <i>s</i> -triazine                        | TNBA                 | 3,3,3-Trinitrobutyric acid  |
| N5 propellant | Ingredients: NC, NG, 2-NDPA, DEP                                   | TNDA                 | 1,3,5,5-Tetranitrohexa-hydropyrimidine (or DNNC)                                    |
| NAT           | Nitroaminotetrazol   | TNDBN                | 1,3,5,7-Tetranitro-3,7-diazabicyclo-[3.3.1]nonane                                   |
| NC            | Nitrocellulose   | TNDPTP               | Tetranitro-dipyridotetraazapentalene  |
| N-DNAZ        | Nitroso-DNAZ   | TNM                  | Trinitromethane   |
| NDPA          | Nitrodiphenylamine   | TNPAN                | Trinitropropylammonium nitrate  |
| NG            | Nitroglycerine   | TNSD                 | 1,3,7,9-Tetranitro-1,3,7,9-tetraazaspiro[4.5]decane                                 |
| NMMO          | 3,3-(Nitratomethyl) methyloxatane                                  | TNSU                 | 2,4,8,10-Tetranitro-2,4,8,10-tetraazaspiro[5.5]undecane                             |
| NQ            | Nitroguanidine   | TNT                  | Trinitrotoluene   |
| NTO           | 3-Nitro-1,2,4-triazol-5-one  | TNTO                 | Tetranitro-3,3,7,7-tetrakis-(trifluoromethyl)-2,4,6,8-tetraazabicyclo[3.3.0] octane |
| NTP           | Nitrotetrazolo[1,5- <i>a</i> ]pyridines                            | TRDX                 | Hexahydro-1,3,5-trinitroso- <i>s</i> -triazine                                      |
| OHMX          | 1,7-Dimethyl-1,3,5,7-tetranitrotrimethylenetetramine               | S                    | Sulfur  |
| ONDO          | 1,1,1,3,6,8,8,8-Octanitro-3,6-diazaoctane                          | XM39                 | RDX (76%)   |
| PA            | Picric acid  |                      |   |
| P-AMMO        | Poly(azidomethylmethyl oxetane)                                    |                      |   |
| P-AZOX        | Poly(azidooxitane)   |                      |   |
| P-BAMO        | Poly(bis(azidomethyl)methyl oxetane)                               |                      |   |
| P-BNMO        | Poly(bis(nitrato)methyloxetane)                                    |                      |   |
| P-DAPMMO      | Poly(diazidopropoxymethyl methyl oxetane)                          |                      |   |

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|  |   |  |  |  |
|--|---|--|--|--|
| 1. AGENCY USE ONLY (Leave blank)   |   | 2. REPORT DATE<br>December 2002                            | 3. REPORT TYPE AND DATES COVERED<br>Reprint, April 2001–March 2002 |  |
| 4. TITLE AND SUBTITLE<br>Applications of Vibrational Spectroscopy in the Study of Explosives   |   |  | 5. FUNDING NUMBERS<br>622618.H80                                   |  |
| 6. AUTHOR(S)<br>Kevin L. McNesby and Rose A. Pesce-Rodriguez   |   |  |  |  |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)<br>U.S. Army Research Laboratory<br>ATTN: AMSRL-WM-BD<br>Aberdeen Proving Ground, MD 21005-5066   |   |  | 8. PERFORMING ORGANIZATION<br>REPORT NUMBER<br>ARL-RP-62           |  |
| 9. SPONSORING/MONITORING AGENCY NAMES(S) AND ADDRESS(ES)   |   |  | 10. SPONSORING/MONITORING<br>AGENCY REPORT NUMBER                  |  |
| 11. SUPPLEMENTARY NOTES<br>A reprint from the <i>Handbook of Vibrational Spectroscopy</i> , J. M. Chalmers and P. R. Griffiths (eds.), Chichester, England: John Wiley & Sons Ltd., 2002.  |   |  |  |  |
| 12a. DISTRIBUTION/AVAILABILITY STATEMENT<br>Approved for public release; distribution is unlimited.  |   |  | 12b. DISTRIBUTION CODE   |  |
| 13. ABSTRACT (Maximum 200 words)<br>A summary of applications of vibrational spectroscopy to the study of explosives is provided. Each application is briefly discussed, and energetic materials studied by that method are listed, with appropriate references. A glossary of the names of explosives is also provided. |   |  |  |  |
| 14. SUBJECT TERMS<br>energetic materials, review, vibrational spectroscopy, explosives, explosives glossary, explosives classification   |   |  | 15. NUMBER OF PAGES<br>22  |  |
|  |   |  | 16. PRICE CODE   |  |
| 17. SECURITY CLASSIFICATION<br>OF REPORT<br>UNCLASSIFIED   | 18. SECURITY CLASSIFICATION<br>OF THIS PAGE<br>UNCLASSIFIED | 19. SECURITY CLASSIFICATION<br>OF ABSTRACT<br>UNCLASSIFIED | 20. LIMITATION OF ABSTRACT<br>UL                                   |  |